

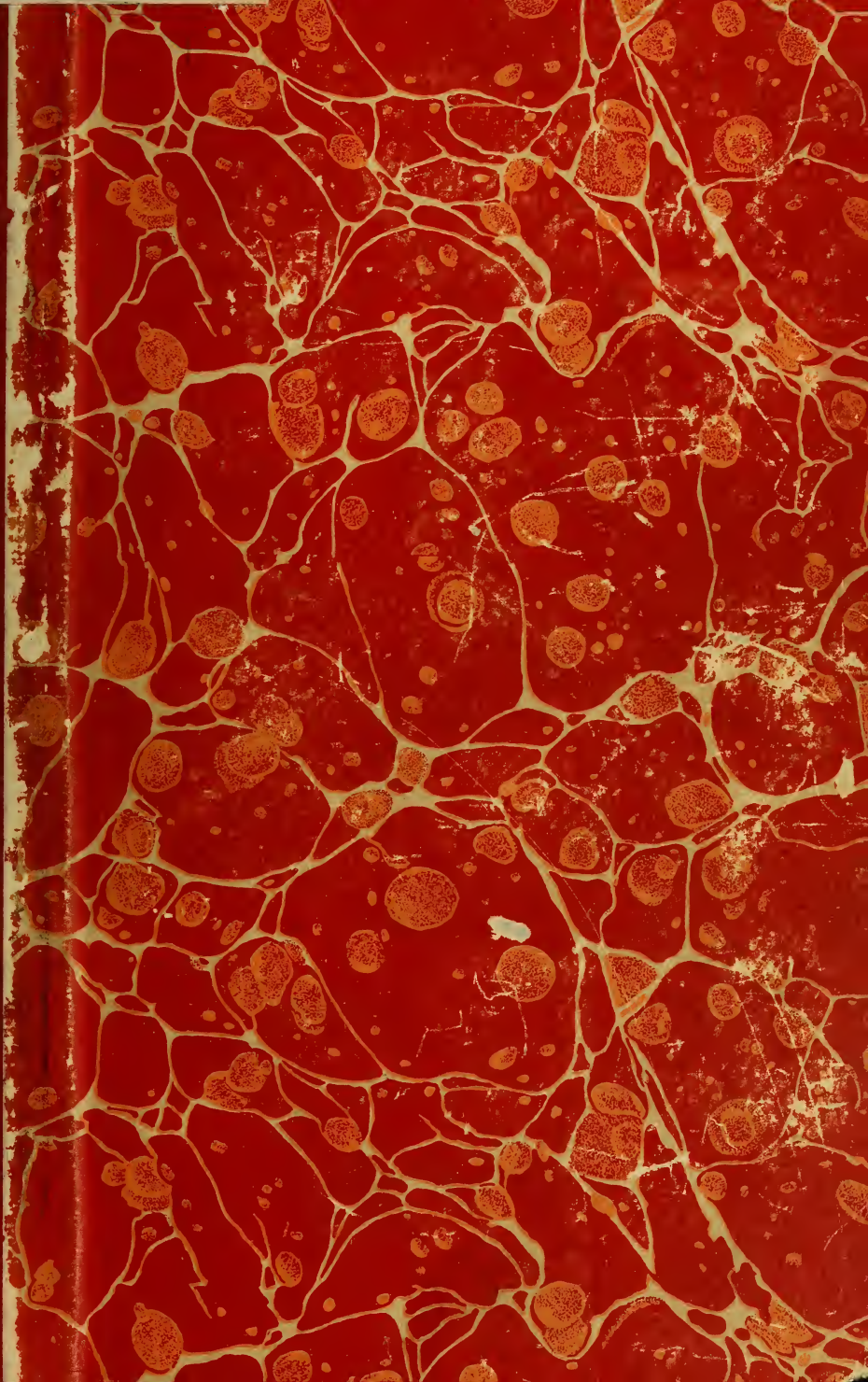
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HEAT OF HYDRATION OF PORTLAND CEMENT PASTES

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ABSTRACT

When water is added to portland cement, heat is liberated, the rate and amount being a function of the composition of the cement. The heats of complete hydration have been determined of the four major compounds of portland cement, $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. By the use of these values, and determinations of the heat of hydration which has occurred at any age, the percentage of the total available heat that has been liberated at that age may be computed. Two methods are described for use in obtaining the heats of hydration; one for ages up to 48 hours and the other for any age of paste greater than 1 day.

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I. INTRODUCTION

When water is mixed with portland cement, reactions take place as a result of which heat is evolved. Under usual conditions of concrete construction, the heat is dissipated rapidly by radiation and temperature changes within the structure are but slight and probably of little consequence. But in concrete structures of very large mass, the heat is not readily radiated and, especially under hot climatic conditions, the mass of the concrete may attain high temperatures. These temperature rises cause expansion while the cement is hardening, and may result in contractions and cracking when the eventual cooling to the surrounding temperature takes place.

Again, during construction in cold weather, special care must be exercised in the placing of concrete to insure that the grout does not freeze. Since the reactions of hydration evolve heat, they are capable of producing a degree of autoprotection against an outside temperature which might otherwise cause freezing or an inhibition of the hardening process.

For each of the above conditions of construction it is desirable that information be available on the total quantity of heat which

may be evolved from the cement and especially on the rate at which this heat is liberated. The present investigation was undertaken to determine the influence of the cement constitution, surface area and temperature on the quantity and rate of heat evolution from cements.

It appears that the processes occurring in portland cement pastes which affect the quantity and rate of heat evolution may be divided into two major classes: the heat liberated (or absorbed) by solution of the anhydrous materials, and the heat liberated (or absorbed) by the precipitation of hydrates from solution. The problem is simplified, however, since, algebraically, the heat of solution of the anhydrous materials, plus the heat of precipitation of the hydrates, is equal to the heat of hydration. The term "hydration" as herein used is the more general expression which includes whatever of hydrolysis may have occurred in any particular case. The precipitation of hydrates cannot lag appreciably behind the solution of anhydrous materials, since the compounds involved are but slightly soluble. Hence the net heat evolved at any given age following the set of the paste is due almost entirely to the hydration which has taken place up to the time of test.

The materials selected for study included the major cement compounds (1)¹, tricalcium silicate, beta dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite, a number of laboratory cements prepared from commercial raw materials and burned in an experimental rotary kiln to give clinkers of systematically varying compositions, a number of commercial cements, and several definite particle size fractions obtained from one of the commercial cements.

II. PREPARATION OF THE CEMENT AND CEMENT COMPOUNDS

The cement compounds used in this investigation were prepared from chemically pure oxides and burned in an up-draft, gas-fired kiln in the manner described in a previous report (2).

The laboratory clinkers² were prepared from commercial raw materials burned in an 8-foot, gas-fired rotary kiln. The temperatures used in making these cements were the minimum temperatures required to obtain complete, or nearly complete, combination as determined by free lime tests (3). Gypsum was added to the cement clinkers to give 1.8 percent SO_3 and the cements were ground in a laboratory pebble mill to such fineness that 87.5 ± 0.5 percent passed the no. 200 sieve.

The commercial clinkers were obtained from the manufacturers. One of these was ground in a laboratory mill to the desired fineness and several particle size fractions separated from the ground clinker by air elutriation. Cements for test purposes³ were made from the clinker fractions and the clinker as ground by the addition of 2.5 percent of gypsum. The clinker and gypsum were placed together in a small pebble mill with a very light charge of flint pebbles and the mill rotated for 15 minutes to accomplish intimate mixing.

¹ Figures in parentheses here and throughout the text and tables refer to the references at the end of the paper, p. 664.

² These clinkers and cements were prepared by W. C. Taylor, of the Portland Cement Association Fellowship.

³ Obtained through the courtesy of R. Wilson, conservation engineer of the Portland Cement Association.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

Two methods were used to determine the heat of hydration of cement pastes: 1, the heat of hydration was calculated from the differences in the heats of solution, in a suitable solvent, of the hydrated and unhydrated cement pastes, and 2, the heat of hydration was measured directly.

1. APPARATUS AND PROCEDURE FOR HEATS OF SOLUTION

The calorimeter used for measuring the heats of solution was designed by R. S. Jessup and P. Rapp in 1925 to measure the heat of hardening of cement pastes and was later modified by W. Lerch and F. C. Hornibrook for heats of solution. The water jacket of the calorimeter, of 2,500-ml capacity, was constructed of nickel-plated brass. The jacket contained a well 13 cm deep and 10 cm in diameter to receive the calorimeter vessel and was provided with a cover 2 cm thick connected to the jacket in a manner that provided circulation of water from the jacket reservoir through the cover. Circulation of the water was effected by a motor-driven rotary stirrer made of brass. A nicrome-wire coil, of 15 ohms resistance, connected through a variable resistance to a 220-volt alternating-current line, provided the means of heating the water in the calorimeter jacket.

The calorimeter vessel was a cylindrical brass vessel of 500-ml capacity, plated with gold and provided with a bakelite cover 1.5 cm thick containing a groove 0.5 cm deep fitting snugly over the rim of the vessel. The air space between the calorimeter vessel and its containing well in the water jacket was 1 cm in width. The stirring of the liquid in the calorimeter vessel was effected by a motor-driven rotary stirrer. The shaft of the stirrer was so constructed that it made an airtight joint where it passed through the brass tube in the cover of the calorimeter jacket, eliminating diffusion of air between the calorimeter and its environment.

The calorimeter was operated adiabatically and observations of the temperature differential between the liquid in the calorimeter vessel and the water in the surrounding jacket were made by means of a five-junction copper-constantan differential thermoelement connected to a Leeds and Northrup galvanometer with scale. The thermoelement junctions were placed in a 0.5-cm glass tube, sealed at one end, the tubes then filled with paraffin, one tube immersed in the liquid of the calorimeter vessel and the other tube in the water reservoir of the jacket. When the jacket temperature became too low, as indicated by the reading on the galvanometer scale, heat could be supplied by means of the heating coil in the jacket. If the jacket temperature became too high, cold water could be added to the jacket to bring about the necessary temperature drop.

Temperature measurements of the liquid in the calorimeter vessel were made by the use of a calibrated five-junction copper-constantan thermoelement junction connected to a galvanometer and a type K Leeds and Northrup potentiometer. The thermoelement junctions were placed in glass tubes in the manner previously described, one tube being immersed in the liquid in the calorimeter vessel, the other

tube being immersed in an ice bath. It was estimated that the differential temperature readings taken in this manner are correct to 0.005°C over the range required.

The stirrer, glass-tube containers, and the heating coil immersed in the liquid in the calorimeter vessel were coated with a cellulose lacquer to protect them from attack by the solution. For the acid solutions used in this investigation, the lacquer provided an excellent protection.

The heat capacity of the calorimeter, with the vessel containing 350 g of solution, was determined with electrical energy. The amount of electrical energy input in any given experiment was computed from the time, which was measured with 0.2-second stop watch, the resistance of the constantan-wire heating coil, which was 20.04 ohms, and the current flowing through the heating coil, which was determined by measuring the potential drop across a standard 1-ohm coil in series with the heating coil.

The heat-capacity experiments were carried out in the following manner: The apparatus was assembled, the stirrers set in operation, and the temperature of the calorimeter vessel and the jacket adjusted to the same initial value of $25 \pm 0.5^{\circ}\text{C}$. After equilibrium was established, observations of the calorimeter temperature were made in a 15-minute "fore" period. In the 15-minute calorimetric "reaction" period, electrical energy was supplied for about 5 minutes, allowing 10 minutes for equilibrium to be established. And finally observations of the calorimeter temperature were made in a 15-minute "after" period. The corrected calorimetric temperature rise was taken as equal to the observed rise in temperature of the calorimeter from the beginning to the end of the reaction period less the average of the temperature changes which occurred in the fore and after rating periods.

A similar procedure was followed in the heat of solution experiments, with the electrical energy being replaced by the energy evolved on dissolving the cement in the solution. In the calorimetric reaction period, the calibrated thermoelement was removed from position and replaced by a funnel through which the cement, whose temperature was $25.0 \pm 0.5^{\circ}\text{C}$, was added at a more or less uniform rate for about 5 minutes. Then the funnel, the end of which extended to about 1 cm above the surface of the solution, was removed and the thermoelement replaced. In the heat of solution experiments 3 g of cement, calculated on the water-free basis, were used. The amount of solution was 350 g less that amount of water which would be added in the cement.

The electrical energy supplied for the determination of the heat capacity was approximately 2,400 cal which gave a temperature rise of about 7°C . The heat of solution obtained from the cements and hydrated materials varied from 1,450 to 2,200 cal and the temperature rise varied in these experiments from 4.2 to 6.3°C .

A preliminary investigation of the solubility of portland cement and the cement compounds indicated the necessity of using different acid solutions for dissolving these several materials. The solvents selected for the solution of the cement compounds, the cements, and their hydration products were: For tricalcium aluminate, a two-normal nitric acid solution; for tetracalcium aluminoferrite, a two-normal

hydrochloric acid solution; and for the calcium silicates and cements, a solution of two-normal nitric and 0.25 normal hydrofluoric acids. With these solvents complete solution was attained in each case.

2. APPARATUS AND PROCEDURE FOR DIRECT HYDRATION

The calorimeter used for measuring the heats of hydration directly was that employed by P. Rapp and C. H. Jumper (4) for measuring the changes in temperature of cement pastes during setting and adopted by W. Lerch and R. Briant for determining heat of hydration. The procedure in the present experiments was as follows: The cement and water were thoroughly mixed in a small tin can, copper-constantan thermoelements inserted in the paste and the can placed in a double-walled vacuum flask which was tightly stoppered with a cork stopper. The thermoelements were connected to a recording potentiometer which recorded the temperature of the cement paste at 15-minute intervals.

During the experiments described in this report, the apparatus was set up in a constant temperature room at $21 \pm 1^\circ\text{C}$ ($70 \pm 2^\circ\text{F}$), and all materials were brought to room temperature before starting an experiment. The water was placed in the tin can, the cement was then added and thoroughly mixed with the water by a mechanical stirrer. The stirring was continued for 1 minute to insure complete and homogeneous mixing of the paste. Three thermoelement junctions were inserted and distributed through the mass of the paste in order to obtain a representative average temperature.

From the data obtained in this manner, the heat evolved by the cement from the beginning of the reaction to any given time can be calculated. The total heat evolved at any given time is equal to the heat absorbed by the calorimeter and contents plus the heat lost by radiation to the surroundings. For this calculation, it is necessary to know the heat capacity and the initial and final temperatures of the calorimeter and contents, and the rate of loss of heat by radiation from the calorimeter.

The heat capacity of the calorimeter was taken as equal to that of the inner wall of the vacuum flask (computed from its mass and specific heat) plus the heat capacity of the tin can, plus the heat capacity of the cement paste (calculated as 0.2 and 1.0 cal per degree for the cement (5) and water, respectively). The radiation-loss constant was determined for each vacuum flask by observing the rate of cooling of a definite quantity of hot water in the tin can placed in the flask.

In each experiment 200 g of cement and 67 g of water were used.

For periods of time longer than 48 hours, this method is not practicable because of the small temperature difference which then exists between the calorimeter and its surroundings.

A number of determinations were made with two commercial cements to determine the reproducibility of the results by this method. In 16 experiments (8 each on 2 cements) the average deviations from the mean values were ± 3.2 and 3.0 percent—or ± 1.8 and 2.0 cal per g, respectively. The total heats per gram were 57 and 68 cal, 46 and 55 of which were computed from radiation and 11 and 13 from the temperature rise of the calorimeter.

IV. HEAT EVOLVED ON COMPLETE HYDRATION

The ultimate quantity of heat that can be liberated by a cement, in the absence of secondary reactions, is that quantity which is evolved on the complete hydration of the constituent compounds to the equilibrium condition imposed by the conditions of the test. A knowledge of the heats of complete hydration of the cement compounds permits the computation of the percentage of the total available heat that has been evolved at any age of test. Accordingly, the heats of complete hydration of the cement compounds and of a number of clinkers were determined.

In the preparation of the hydrated materials, the respective compounds and cement clinkers were ground to an impalpable powder and water was added in sufficient quantity to produce a paste of approximately normal consistency (6). The pastes were thoroughly mixed and placed in an Erlenmeyer flask which was then tightly stoppered and sealed with paraffin wax. These pastes were allowed to hydrate at room temperature for about 1 month. At that time the flasks were broken away from the hardened pastes, the latter were reground and mixed with sufficient additional water to again give a plastic paste. These mixtures were allowed to continue their hydration as before. The hardened pastes were reground twice at subsequent intervals and treated in a similar manner. After this treatment microscopic and X-ray examination of the hydrated compounds failed to reveal the presence of the unhydrated compounds, except in the case of beta dicalcium silicate which still contained a small amount of unhydrated material, estimated to be about 2 or 3 percent. Reexaminations of the hydrated compounds at later ages have shown no appreciable changes in the heat values obtained as described and reported below.

It should be pointed out that the term "complete hydration" as used in this investigation refers to a limiting condition of hydrolysis and hydration which the cement compounds in mortars and concretes may be expected to approach but never to exceed. It is for this reason that the values were obtained under conditions of water concentration similar to those encountered in mortars and concretes rather than in an excess of water. Hence the values given may not in all cases denote the theoretical equilibrium condition. As an example, it may be mentioned that the composition of the calcium silicate in equilibrium with saturated calcium hydroxide was found to be $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$. But in mortars the hydrolysis has not been found to proceed appreciably beyond the composition $2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$. Hence the values given for the "complete hydration" of $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ represent the heats liberated on conversion to $2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ rather than to the hypothetical equilibrium composition of $3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

The results obtained from this phase of the investigation are given in table 1. The data presented in the table include the composition of the materials examined, the heat of solution of the anhydrous materials, the heat of solution of the hydrated materials on the ignited basis, the heat evolved on complete hydration, obtained by the difference between these two and, in the case of the cement clinkers, the calculated heat of hydration computed from the compound composition of each clinker.

TABLE 1.—Heat evolved on complete hydration of cement compounds and portland cement clinkers

	Partial analyses of cement compounds and of cement clinkers						Computed compound composition of cement clinkers						Heat anhydrous materials	Hydrated materials on ignited basis	Heat evolved on complete hydration	Calculated heat of hydration	Difference between experimental and calculated values
	CaO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	MgO	B ₂ O ₃	C ₃ S	C ₂ S	C ₃ A	C ₄ A	MgO	Free CaO					
Pure compounds																	
C ₃ A	62.3	37.9	0.05	0.01					100				cal/g 733	cal/g 526	cal/g 207	cal/g	Percent
C ₄ A	46.3	20.8	33.0	0.03						100			519	419	100		
C ₃ S	73.8	.1	.06	25.8			100						632	512	120		
βC ₂ S	65.1	.1	.06	34.4		0.4	100						563	501	62		
CaO (7)													828.9	550.3	278.6		
MgO (8)													862	659	203		
Clinkers, series K-3																	
No. 4	63.7	4.0	4.9	23.9	3.1		44	36	2	15	3.1	0	623	526	97	100	+3.1
No. 5	64.7	7.0	2.0	22.1	3.7		46	29	15	6	3.7	0	649	523	126	118	-4.8
No. 15	66.6	7.4	1.7	19.8	4.0		62	10	17	5	4.0	1.5	666	521	145	133	-8.3
No. 17	65.4	5.4	5.5	20.0	3.3		69	5	5	17	3.3	0	638	519	119	120	+0.8

It is shown that the heats of complete hydration of the cement compounds, as obtained in this study, are as follows:

Tricalcium aluminate	cal/g	207
Tetracalcium aluminoferrite	do	100
Tricalcium silicate	do	120
Beta dicalcium silicate	do	62

Four determinations were made on each compound. The probable error of the determination is computed to be ± 3 cal per g.

The values given for lime (7) (278.6 cal per g) and magnesia (8) (203 cal per g) were available in the literature and were not redetermined in this investigation.

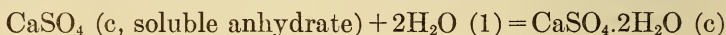
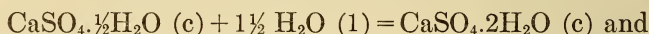
The heat of hydration of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ to $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ has been reported by Thorvaldson (7) as 214.3 cal per g. Considering the difficulties involved in preparing these compounds in pure form, this value is in good agreement with results obtained in the present investigation.

The values obtained for the complete hydration of the cement clinkers shown in table 1 are in fair agreement with the values for complete hydration computed from the compound composition of the clinkers. The values obtained for the heat of solution of the anhydrous and hydrated clinkers are larger than the values which would be obtained from calculations using the heat of solution of the several compounds as given in the table. This is probably due to the use of different solvents in determining the heat of solution of the several cement compounds. However, the heats of hydration of the clinkers when calculated by this method are identical with the calculated values obtained from the heat of hydration factors of the individual compounds. The percentage differences between the experimental and the computed values are shown to range from +3.1 to -8.3, the experimental value being taken as the basis of comparison. It

cannot be stated at this time if these divergencies are due solely to experimental error or if they involve some inherent characteristics of the cement clinkers whereby the latter differ slightly from the cement compounds when prepared separately. However, these differences are relatively small.

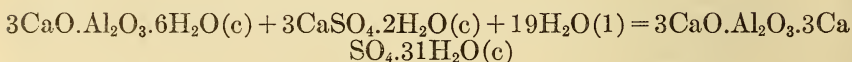
The generally satisfactory agreement between experimental and computed heats of complete hydration leads to the belief that secondary reactions, if they occur on the hydration of clinkers, are relatively insignificant so far as heat transfer is concerned and that the total heat available on the hydration of a clinker may be computed with a fair degree of precision from the heats of hydration of the constituent compounds.

The only essential difference in composition between a clinker and a cement is the presence of calcium sulfate in the latter. This is usually added to the clinker in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) but, during the grinding process, the gypsum may have been partially or completely dehydrated to plaster ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) or soluble anhydrite (CaSO_4), respectively. The calcium sulfate has been found to react with tricalcium aluminate hydrate during set or early hardening to form calcium sulfoaluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$). In computing the total heat available from the hydration of a cement it is accordingly necessary to consider the heat involved in the hydration of the plaster or anhydrite and the heat involved in the reaction of the hydrated gypsum with the hydrated tricalcium aluminate to form calcium sulfoaluminate. For the reactions



the heats evolved are, respectively, 3.7 and 2.7 kcal per mol, (9) or 46 and 34 cal per g SO_3 . With the usual percentages of calcium sulfate in cement, this represents a heat value of about 1 cal per g of cement. Inasmuch as the extent of dehydration of the gypsum during grinding is a variable and indeterminate quantity and the heat involved is slight, it appears best to avoid the introduction of a heat factor for the calcium sulfate hydration in the computations of total available heat from cements.

The heat liberated by the reaction



was computed to be about 149 cal per g of SO_3 . This calculation was made from data obtained in the present investigation on the heats of solution of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}(c)$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}(c)$ in aqueous HCl and from the data on $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(c)$ given in the International Critical Tables. Since the foregoing reaction has been found generally to occur during the setting process or shortly thereafter, and the value is significant, it appears proper to take it into consideration in the computations of total heat available on the complete hydration of cements. This has been done in the computations appearing in tables 2 and 3 referred to later in the paper.

V. THE RATE OF HEAT EVOLUTION AT EARLY AGES BY THE DIRECT HYDRATION METHOD

A large number of cements have been examined by the direct hydration method to determine the quantity of heat evolved at ages up to 48 hours. By this method it was possible to calculate the heat evolved at hourly intervals. Some of these results are presented in the accompanying figures which show the values obtained during the first 24 hours.

The materials examined in this part of the investigation included 61 laboratory cements prepared from commercial raw materials to give clinkers of systematically varying composition and 10 commercial

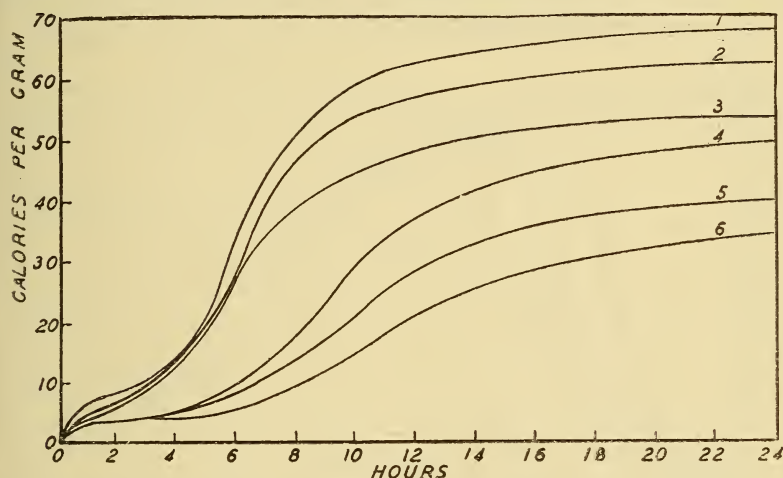


FIGURE 1.—Heat evolution from cements in which $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ are the major variables.

No.	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	C ₂ F	MgO	Free CaO
1	43	30	18	4	0	2.8	1.4
2	47	26	16	7	0	3.0	.3
3	43	33	11	10	0	3.1	.3
4	43	34	7	13	0	3.1	0
5	39	40	2	16	0	3.1	.1
6	41	39	0	14	3	3.0	0

clinkers. Gypsum was added to give 1.8 percent SO_3 and the materials ground to such fineness that 87.5 ± 0.5 percent passed the no. 200 sieve.

In the case of the laboratory cements, the raw materials were proportioned with the intent of varying certain compounds in the clinker and maintaining the other compounds constant. The clinkers were analyzed, including the free lime determination, and the compounds computed. Although the final computations showed that compositions were not precisely as designed, the nature of the effects of composition on rate of heat liberation is clearly indicated.

The results obtained on cements wherein the tricalcium aluminate was decreased by substituting ferric oxide for alumina are shown in figure 1. These results indicate that each decrease in the tricalcium aluminate content is accompanied by a decrease in the quantity of heat liberated during the first 24 hours. (In the figures and tables

abbreviations in the formulas of the compounds have been used as follows: $C_3S = 3CaO.SiO_2$; $C_2S = 2CaO.SiO_2$; $C_3A = 3CaO.Al_2O_3$; $C_4AF = 4CaO.Al_2O_3.Fe_2O_3$.)

Figure 2 shows the effect of decreasing the tricalcium silicate and increasing the dicalcium silicate with all other factors substantially constant. These results indicate that each decrease in the tricalcium silicate content is accompanied by a decrease in the quantity of heat liberated during the first 24 hours, with the exception of cement no. 57. This cement contained 2.1 percent free lime, a compound which hydrates rapidly and liberates a large quantity of heat per unit weight.

The results obtained with cements in which the magnesia content is varied are shown in figure 3. In these cements the tricalcium

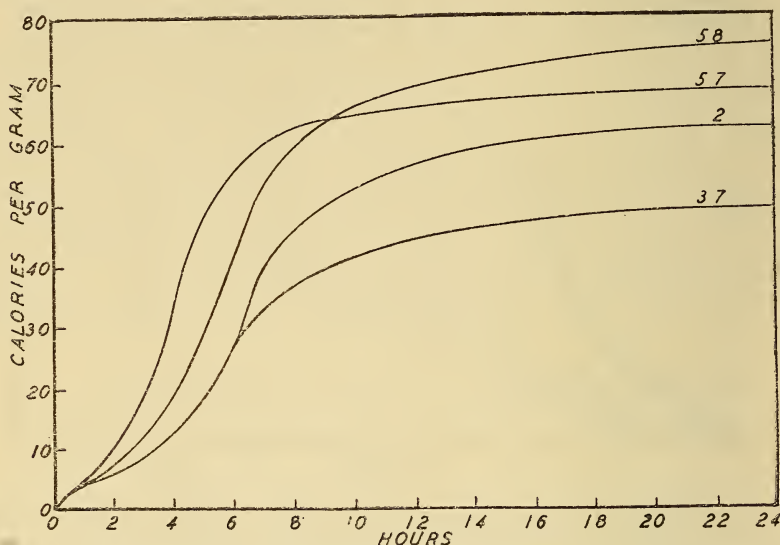


FIGURE 2.—Heat evolution from cements in which $3CaO.SiO_2$ and $2CaO.SiO_2$ are the major variables.

No.	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO
58	62	13	14	7	3.3	0.7
57	45	28	15	7	2.9	2.1
2	47	26	16	7	3.0	.3
37	16	58	16	6	3.0	.2

aluminate and tetracalcium aluminato ferrite were maintained constant and the calcium oxide and silica were adjusted to maintain a substantially constant tricalcium silicate content. Thus, the dicalcium silicate decreased as the magnesia increased. Varying the magnesia content in this manner results in only slight differences in the quantity of heat liberated at 24 hours and the results show no definite trend with relation to the magnesia content.

The heat data from three commercial cements which were ground in a laboratory mill to 3 degrees of fineness have shown that the rate with which the heat is liberated increases with increased fineness. The data on one of these cements are plotted in figure 4. The other two cements gave similar results. It is observed that the reaction occurs earlier with the finer cements but that, at 24 hours, the total amount of heat evolved is not greatly different for the different

degrees of grinding. At 48 hours the differences became even smaller.

Still other factors which have been found to contribute to the differences in the rate of heat evolution at very early ages are the temperature of the paste during hydration, the water/cement ratio and the quantity of retarder present. The effects of these factors, however, become small after 48 hours.

The curves presented in this report, showing the heat evolved at various time intervals, are of interest in a consideration of the processes occurring during the setting and hardening of the cement. In general, the curves contain four distinct phases. There is an initial rise in the temperature with all compositions, which occurs during the

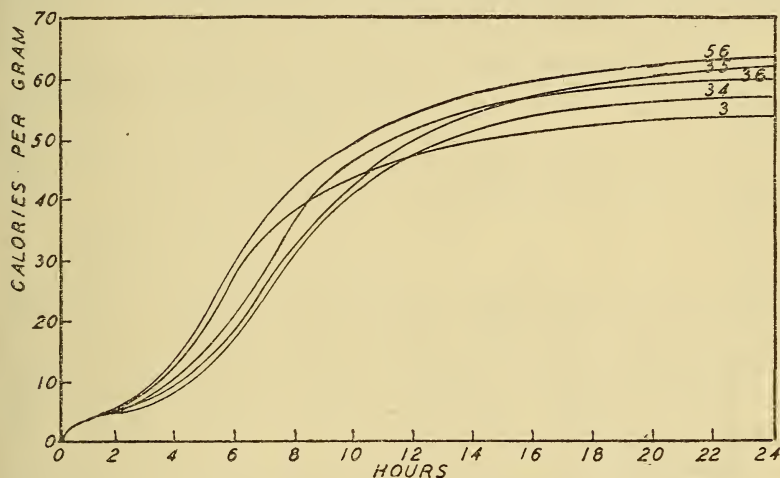


FIGURE 3.—Heat evolution from cements in which MgO and $2\text{CaO} \cdot \text{SiO}_2$ are the major variables.

No.	C_3S	C_2S	C_3A	C_4AF	MgO	Free CaO
56	47	23	11	9	9.9	0.1
35	41	33	11	9	4.9	.2
36	42	30	11	9	7.0	.3
34	41	36	11	9	1.4	.2
3	43	33	11	10	3.1	.3

first few minutes. This is followed by a period in which there are only slight thermal changes; the duration of this period varies from a few minutes to several hours depending on the composition of the cement. In the third phase there is a rapid evolution of heat followed by the fourth phase wherein the thermal changes become relatively slow.

The initial rise appears to be due to the heat of wetting, the mechanical heat of stirring, and probably in part to the heat of solution. This is indicated by the observation that the maximum temperature of this period has been reached in the first few minutes, that is, by the time the first temperature reading is recorded.

The next period, in which there is a very slow evolution of heat, is a period in which it appears that the water is becoming saturated with the various compounds of the cement. The rate of solution is then dependent on the relative solubility of the various compositions used, on the fineness of the cement, and on the temperature of the paste during this period.

The period of rapid evolution of heat appears to be a period of rapid solution of anhydrous material and precipitation of hydrated material. The algebraic sum of these processes for the compounds of cement is, at this stage, highly exothermic. It has been observed that the beginning of this period of rapid evolution of heat occurs at about the same time period as that at which the initial set takes place (4). The layer of hydrated crystals and amorphous hydrated material, deposited around the unhydrated portion of the grains, as also the depletion of the solvent, tend to retard the further penetration of water and hydration of the cement. This results in a diminution in the rate of evolution of heat in the succeeding periods, even though the hydration has not approached completion in that time.

A number of observations support these postulations. A microscopic study of the process of hydration of tricalcium aluminate and

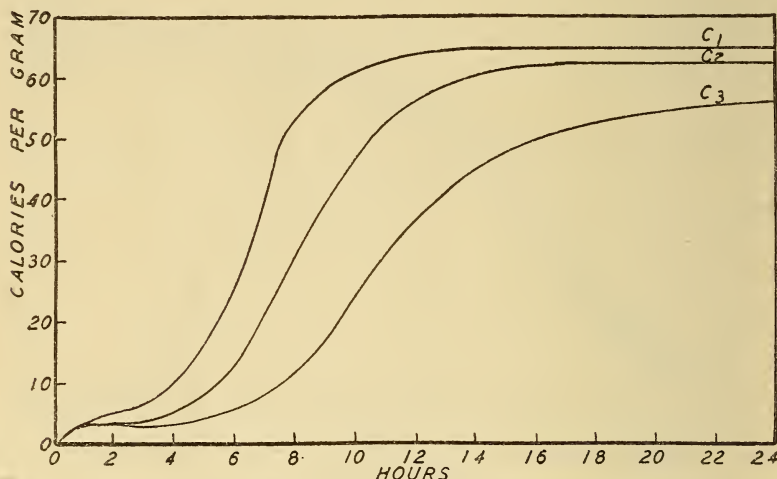


FIGURE 4.—Heat evolution from a cement ground to different degrees of fineness.

No.	Percent passing no. 200 sieve
C ₁	96
C ₂	89
C ₃	83

tetracalcium aluminato ferrite gives evidence of the formation within a few minutes of crystals of a hydrated phase. This would lead to the conclusion that these materials dissolve rapidly which is in agreement with the nature of the data obtained with those materials. The microscopic examination of hydrating tricalcium silicate indicates that several hours are required for the first crystals of calcium hydroxide to appear and for the first evidence of colloidal hydrate formation. The experiments with beta dicalcium silicate show no evidence of this period of rapid evolution of heat.

Hence, changes in composition of the cement whereby the more soluble compounds are diminished may be expected to prolong the period of quiescence which precedes the rapid rise in temperature. That condition is especially noticeable in the cements in which the tricalcium aluminate is decreased, and is noticeable to a lesser degree in cements in which tricalcium silicate is decreased. Likewise, in accordance with the above theory, acceleration of the reactions by the

physical methods of finer grinding of the cements and higher initial temperature is found to advance the period of rapid heat evolution.

All of the heat data obtained on the laboratory cements at 48 hours were subjected to a mathematical analysis by the method of least squares. As a result of this analysis it became apparent that the heat liberated by the hydration of the free CaO could not be observed when the percentage of free CaO present was not greater than about 0.5 percent. The heat liberated by CaO on complete hydration at 20 C was found by Thorvaldson, Brown, and Peaker (7) to be 278.6 cal/g. Thus, the presence of 0.5 percent free CaO in clinker would, on complete hydration, contribute 1.4 cal/g of clinker at 20 C (68 F), which is less than the probable error of the method. Also, the magnesia was found to be without appreciable effect at 48 hours and the effect of the dicalcium silicate could not be evaluated because of the very small amount of heat evolved by that compound at early ages.

A solution of the normal equations, in which tricalcium aluminate, tricalcium silicate, and tetracalcium aluminoferrite were assumed to be responsible for all of the heat evolved at 48 hours, produced the following values, representing the heats of hydration at 48 hours contributed by each percent of the above compounds per gram of cement:

Tricalcium aluminate.....	1.50
Tricalcium silicate.....	1.00
Tetracalcium aluminoferrite.....	.40

Inasmuch as cement compositions are often reported only in terms of the oxide components, it may sometimes be desirable to interpret the heat data in terms of the oxides. Since the percentages of the compounds present are a linear function of the percentages of the oxides (10) the desired transformations may readily be made. The results obtained for the contribution of each percent of the oxides in the cement to the heat evolution at 48 hours of one gram of cement are as follows:

CaO.....	+4.08
SiO ₂	-7.61
Al ₂ O ₃	-2.75
Fe ₂ O ₃	-2.76

In applying these data to cements, the percentage of lime must be corrected for the lime present in the retarder as calcium sulfate.

On applying the factors given above for the cement compounds to the computation of the heat evolved at 48 hours from the 61 laboratory cements, the calculated and experimental heats were found to agree within a probable error of ± 3 cal/g of cement.

Ten commercial cements of widely varying composition also were examined in a similar manner and equally satisfactory agreement was found between the computed and experimental results.

Since the rate of heat evolution, in contradistinction to the total heat of hydration, is sensibly affected by many variables, such as surface area, temperature, available water, retarder present, thermal history of the clinker, etc., in addition to the composition, the heat factors given above can be considered as applying only under the specific conditions of manufacture and test imposed upon the cements investigated. The value of the data lies in the definite effects indicated, due to changes in the composition with a given set of conditions, and under these circumstances the effect on the rate of heat evolution at early ages due to changes in the percentage of the compounds present is clearly shown.

VI. THE RATE OF HEAT EVOLUTION BY THE HEAT OF SOLUTION METHOD

Several cements were examined by the heat of solution method to determine the quantity of heat evolved at various ages after mixing the paste. For this purpose the cements were thoroughly mixed with 40 percent of water, by weight, and the pastes placed in 1-inch glass vials. The vials were immediately stoppered with corks and sealed with paraffin. The vials were then placed in constant temperature cabinets where they remained until required for the heat of solution determinations. Some of the vials were cured at 25 C (77 F), and others at 35 C (95 F), to compare the rate of evolution of heat at these different temperatures.

TABLE 2.—Rate of evolution of heat from cements of variable composition

Number	1	3	6	8	43S	106	Commercial clinker (c)
Partial oxide composition							
CaO.....	62.7	64.2	64.9	66.6	62.6	66.6	65.7
Al ₂ O ₃	4.0	6.9	3.9	6.8	4.1	7.4	7.0
Fe ₂ O ₃	5.1	2.0	5.0	2.0	4.7	1.7	2.0
SiO ₂	25.5	23.4	22.7	21.0	25.4	19.8	22.1
MgO.....	2.5	3.1	3.1	3.0	2.8	4.0	2.6
Computed compound composition (percent)							
3CaO. SiO ₂	27	31	57	53	27	63	51
2CaO. SiO ₂	53	43	22	20	52	10	24
3CaO. Al ₂ O ₃	2	15	2	15	3	17	15
4CaO. Al ₂ O ₃ . Fe ₂ O ₃	15	6	15	6	14	5	6
MgO.....	2.5	3.1	3.1	3.0	2.8	4.0	2.6
Free CaO.....	0	.6	.1	2.3	0	1.4	-----
Gypsum added.....	3.8	3.8	3.8	3.8	3.8	3.8	2.5
Computed heat available from complete hydration, cal/g							
	91	112	110	128	93	136	120
Heat of hydration, neat cement							
1 day: Cal/g obtained at 25 C.....	35	38	44	49	-----	-----	-----
Cal/g obtained at 35 C.....	-----	-----	-----	-----	38	71	48
Percent of total heat obtained at 35 C.....	-----	-----	-----	-----	41	52	40
2 days: Cal/g obtained by direct method.....	45	64	74	76	42	82	-----
3 days: Cal/g obtained at 25 C.....	49	61	54	74	-----	-----	-----
Cal/g obtained at 35 C.....	51	63	61	82	50	95	67
Cal/g computed at 35 C.....	43	66	66	88	44	90	65
Percent of total heat obtained at 35 C.....	56	56	55	64	54	70	56
7 days: Cal/g obtained at 25 C.....	50	71	67	86	-----	-----	-----
Cal/g obtained at 35 C.....	57	75	73	97	52	105	90
Cal/g computed at 35 C.....	48	73	75	98	49	101	89
Percent of total heat obtained at 35 C.....	63	67	66	76	56	77	75
28 days: Cal/g obtained at 25 C.....	63	82	76	106	-----	-----	-----
Cal/g obtained at 35 C.....	70	93	86	113	70	117	95
Cal/g computed at 35 C.....	63	87	83	105	66	108	99
Percent of total heat obtained at 35 C.....	77	83	78	88	75	86	79
90 days: Cal/g obtained at 25 C.....	74	94	86	114	-----	-----	-----
Cal/g obtained at 35 C.....	76	94	92	117	76	117	101
Cal/g computed at 35 C.....	71	92	90	111	71	112	104
Percent of total heat obtained at 35 C.....	84	84	84	91	82	86	84
180 days: Cal/g obtained at 35 C.....	75	98	93	117	-----	-----	106
Cal/g computed at 35 C.....	73	96	93	115	-----	-----	108
Percent of total heat obtained at 35 C.....	83	88	85	91	-----	-----	88

¹ Computed from factors of Woods, Steinour, and Starke (reference 11).

The results obtained from seven cements are given in table 2. In addition to data on composition and gypsum additions, this table contains the data on heat evolved as obtained by the heat of solution method at ages of 1, 3, 7, 28, 90, and 180 days at temperatures of 25 and 35 C (77 and 95 F). The 2-day values obtained by the direct method also are included. Woods, Steinour, and Starke (11) have computed factors which indicate the contribution of the individual compounds to the heat evolution at ages 3, 7, 28, 90, 180, and

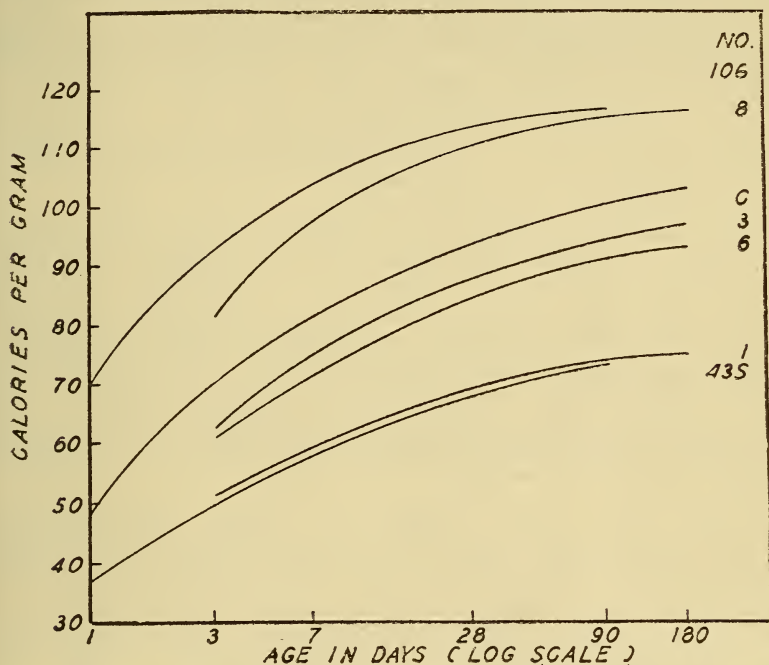


FIGURE 5.—Heat evolution at 35 C from cements of different composition at ages to 180 days.

No.	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	Free CaO
106	63	10	17	5	4.0	1.4
8	53	20	15	6	3.0	2.3
C	51	24	15	6	2.6	—
3	31	43	15	6	3.1	.6
6	57	22	2	15	3.1	.1
1	27	53	2	15	2.5	0
43S	27	52	3	14	2.8	0

365 days. Seventeen laboratory cements of a wide range in composition were used by those investigators, these being ground to about 99.8 percent passing the 200 no. sieve. By the use of these factors, values were computed of heat liberation at corresponding ages for the cements examined. These computed values also are recorded in table 2.

The amounts of heat liberated from the above cements at the ages tested are shown in figure 5.

An examination of the results obtained from these cements confirms the earlier finding that tricalcium aluminate and tricalcium silicate are compounds which contribute large quantities of heat of hydration to the cements at all ages, while the dicalcium silicate and

tetracalcium aluminato ferrite contribute lesser quantities of heat and at a slower rate. Thus cement no. 3 evolves more heat than cement no. 1, and cement no. 8 evolves more heat than cement no. 6 where the major differences in composition are an increase in the tricalcium aluminate content and a decrease in the tetracalcium aluminato ferrite. Also cement no. 6 evolves more heat than cement no. 1, and cement no. 8 evolves more heat than cement no. 3, but in these pairs the major differences in composition are an increase in the tricalcium silicate content and a decrease in the dicalcium silicate content.

The number of cements used in this investigation was not sufficient for a statistical analysis to determine the heat factors for the individual compounds at the different ages of test. However, the calculated values obtained by the use of factors given by Woods, Steinour, and Starke are generally in good agreement with the experimentally obtained values at 35 C. The application of those factors, however, cannot be expected to be quantitative for the reasons given in the discussion of the direct hydration method.

The values obtained by the direct method at 2 days are in fair agreement with the extrapolated values at 35 C obtained by the heat of solution method at 1 and 3 days with one exception. This comparison is not rigid, however, because, by the direct method, the temperature during hydration is not constant, whereas in the heat of solution method, the curing temperatures of the small specimens used remain approximately constant. The general concordance of the results, however, gives assurance of the soundness of the two quite independent methods of examination and permits the extrapolation of data between the early and late periods covered by the two methods.

The amounts of heat available on complete hydration of the cements, as previously defined, have been computed from the compositions and are set down in table 2. By the use of these values, the percentage of the available heat that has been liberated from each cement at each test period has been computed. It is seen that about half of the total available heat is liberated between 1 and 3 days, about three quarters in 7 days, and from 83 to 91 percent in 6 months, when the pastes are cured at 35 C (95 F). It may also be noted that both the total quantity and the rate of heat liberation are greatest with those cements high in tricalcium aluminate and tricalcium silicate.

The amounts of heat evolved at 35 C (95 F) are consistently higher than those evolved at 25 C (77 F), but the magnitude of the difference is not large.

VII. EFFECT OF SURFACE AREA ON RATE OF HEAT EVOLUTION

Several definite particle size fractions obtained from a commercial cement by air elutriation were examined by the heat of solution method to determine the quantity of heat evolved by the different fractions at various intervals. Pastes were prepared from these fractions in the manner previously described and the pastes cured at 35 C (95 F).

The results obtained from these fractions, together with results obtained from the whole clinker as ground, are given in table 3 and

are shown graphically in figure 6. The table gives the particle size of each fraction, expressed both in microns and in terms of the surface area of each fraction in sq cm/g; the oxide composition and the computed compound composition of each clinker fraction; the amount of gypsum added; the calculated heat available from the complete hydration of the cements; the experimentally obtained values of the heat evolved at various intervals; and the values obtained at the various intervals calculated to percent of the total heat available.

This study did not include all of the fractions separated from this cement, but the number examined covers a wide range of particle size

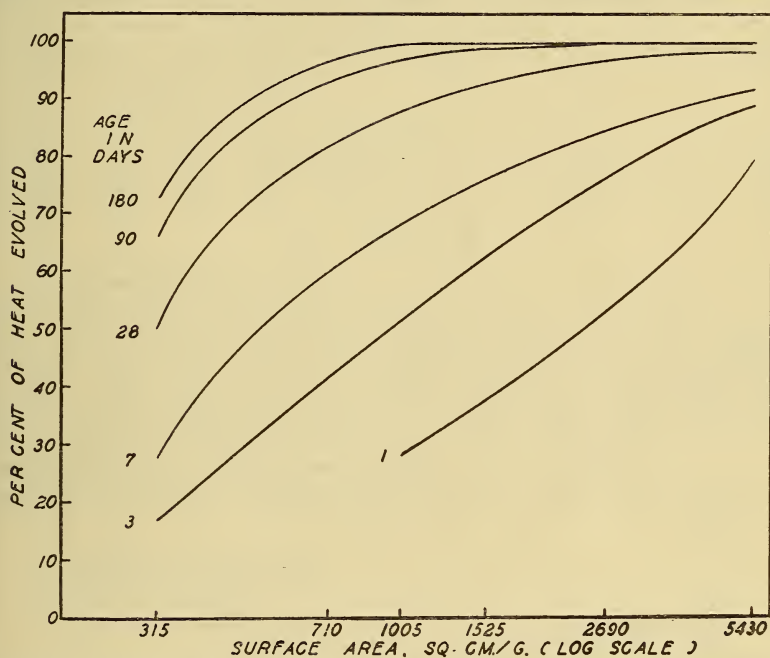


FIGURE 6.—Percentage of total heat evolved from differently sized fractions of a cement at ages to 180 days.

and surface area and was considered sufficient to indicate the effect of particle size on rate of evolution of heat from this cement.

The computed compound composition of the fractions is shown not to be identical, the most pronounced difference being a consistent variation in the calcium silicates present. The tricalcium silicate content decreases and the dicalcium silicate content increases as the particle size increases. This is in agreement with results previously reported by Carlson and Bates (12). These changes in compound composition bring about a progressive decrease, as the particle size increases, in the computed quantity of heat available upon complete hydration.

The results given in table 3 and figure 6 show a pronounced difference in rate of evolution of heat from the variously sized fractions as indicated by the experimentally obtained values, expressed in cal/g; and also as indicated by the computed values showing the percent of the total available heat that has been evolved at each age. Thus,

the 0 to 5 micron fraction had evolved 87 percent of its total heat in 3 days, whereas the 48 to 60 micron fraction had evolved only 17 percent of its heat at that age. At 28 days the fine fraction was almost completely hydrated whereas at that time the coarse fraction was but 50 percent hydrated. The intermediate fractions evolved heat at rates which corresponded to their respective surface areas.

TABLE 3.—Rate of evolution of heat from a commercial cement and from several definite particle size fractions obtained from the cement

Particle size in microns	Less than 5	5 to 10	10 to 16	16 to 20	20 to 30	48 to 60	Whole cement
Surface area, sq cm/g ¹	5, 430	2, 690	1, 525	1, 005	710	315	1, 675
Partial oxide composition							
CaO.....	66.2	66.2	66.2	66.1	65.9	65.1	65.7
Al ₂ O ₃	7.2	6.8	6.5	6.8	7.0	7.4	7.0
Fe ₂ O ₃	2.0	2.0	1.8	1.9	1.9	2.1	2.0
SiO ₂	21.3	21.7	22.3	22.4	22.3	22.3	22.1
MgO.....	2.6	2.5	2.4	2.4	2.4	2.6	2.6
SO ₃3	.2	.2	.2	.2	.2	.2
Computed compound composition							
3CaO.SiO ₂	58	57	55	52	50	45	51
2CaO.SiO ₂	16	18	21	24	25	29	24
3CaO.Al ₂ O ₃	16	15	14	15	15	16	15
4CaO.Al ₂ O ₃ .Fe ₂ O ₃	6	6	6	6	6	6	6
MgO.....	2.6	2.5	2.4	2.4	2.4	2.6	2.6
Gypsum added.....	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Computed heat available from complete hydration, cal/g							
	126	123	120	120	118	117	120
Heat of hydration, neat cement							
1 day: Cal/g obtained at 35 C.....	99	64	44	37	-----	-----	48
Percent of total heat liberated.....	79	52	37	31	-----	-----	40
3 days: Cal/g obtained at 35 C.....	109	88	74	61	47	20	67
Percent of total heat liberated.....	87	72	62	51	40	17	56
7 days: Cal/g obtained at 35 C.....	113	100	85	83	69	31	90
Percent of total heat liberated.....	90	81	71	69	58	27	75
28 days: Cal/g obtained at 35 C.....	120	104	107	101	101	58	95
Percent of total heat liberated.....	95	85	89	84	86	50	79
90 days: Cal/g obtained at 35 C.....	126	120	115	114	109	76	101
Percent of total heat liberated.....	100	98	96	95	93	65	84
180 days: Cal/g obtained at 35 C.....	124	120	118	118	112	84	106
Percent of total heat liberated.....	99	98	99	99	95	72	88

¹Based on calculation from microscopic determinations of diameters.

A small part of the differences in rate of heat evolution may be accounted for by the differences in composition with respect to the calcium silicates. Tricalcium silicate, which is present in the greatest amount in the finer fractions, hydrates more rapidly than dicalcium silicate. This would tend to accelerate the hydration of the finer fractions. However, the differences in heat liberated due to the slight variations in composition appear to be of minor significance in

these separate fractions as compared with the large differences shown to be due to the particle size. This is indicated by the differences obtained for the computed values of the heat available from complete hydration of the several fractions. These variations are relatively small compared to the divergencies in the experimentally obtained values, at early ages, for these various fractions.

It should be pointed out that large differences were observed in the surface areas of the several fractions as computed from microscopic determination of the mean particle sizes. The surface areas varied from 315 sq cm/g in the 48 to 60 micron fraction to 5430 sq cm/g in the minus 5 micron fraction. This explains the large differences in rate of heat evolution obtained on these fractions as compared with the small differences observed after 24 hours of the differently ground cements described in section V. Although surface areas of the cements reported in section V were not determined, a number of tests have shown that the surface areas that may be anticipated by grinding a clinker (in a laboratory mill) to finenesses of 87.5 and 97 percent passing the no. 200 sieve range from about 1,800 to 2,500 sq cm/g.

VIII. SUMMARY

1. The partial and total heats of hydration of portland cement pastes have been determined by two independent methods: 1, by measuring the heat of hydration directly, and 2, by measuring the heats of solution in the same solvent of the hydrated and unhydrated samples. The first, or direct method, utilizes a vacuum flask calorimeter and is applicable for ages up to 48 hours. The second, or indirect method, is applicable for ages of 1 day and longer.

2. The total heats available upon the complete hydration of compounds present in portland cement were found to be as follows:

	cal/g
Tricalcium silicate.....	120
Beta dicalcium silicate.....	62
Tricalcium aluminate.....	207
Tetracalcium aluminoferrite.....	100

In addition, the following values were taken from the literature:

Magnesia.....	203
Free CaO.....	279

The heat of hydration of the calcium sulfate in portland cement, which may have been partially or completely dehydrated during the grinding process, is shown to be inappreciable. The heat of reaction of gypsum and tricalcium aluminate hydrate to form calcium sulfoaluminate is found to be 149 cal/g of SO_3 .

3. By use of the above heat values, the total heat available on the complete hydration of a clinker or cement may be computed from the composition. Experimental values obtained on a number of clinkers were found to be in good agreement with computed values of heat of complete hydration.

4. By use of the computed values representing heat of complete hydration of a cement, together with heat of solution tests of the original cement and of the paste at any desired age, the percentage of the total available heat that has been liberated at any age of test may be computed. Such computations have shown that a relatively large proportion of the total available heat is liberated in a few days but

that the heat may continue to be evolved at a progressively decreasing rate through the later ages.

5. Factors have been computed which indicate the amount of heat contributed by the compounds $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $3\text{CaO} \cdot \text{SiO}_2$, and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ to the total heat liberated during the first 48-hour period after mixing with water. These factors may not be applied rigidly to commercial cements because of indeterminate variables in the latter which affect the rate of heat evolution at early ages, but they may be used under specified conditions of manufacture and test to predict the effect of changes in composition on the rate of heat evolution at early ages.

6. The rate of heat evolution is found to increase as the surface of the cement is increased. With the laboratory-ground cements, herein described, varying in surface area from about 1,800 to 2,500 sq cm/g, differences in fineness resulted in differences in rate of heat evolution during the first few hours after mixing the paste but approached equivalent values in 1 or 2 days. A period of many months may be required, however, to bring about an hydration of a coarse fraction equivalent to that brought about in a finer fraction in a few days.

7. The amounts of heat evolved at 35 C are consistently higher than those evolved at 25 C, but the magnitude of the differences is not large.

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